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Exchange and correlation energy in density functional theory: Comparison of accurate density functional theory quantities with traditional Hartree–Fock based ones and generalized gradient approximations for the molecules Li_2, N_2, F_2

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The density functional definition of exchange and correlation differs from the traditional one. In order to calculate the density functional theory (DFT), quantities accurately, molecular Kohn–Sham (KS) solutions have been obtained from *ab initio* wave functions for the homonuclear diatomic molecules Li_2, N_2, F_2. These afford the construction of the KS determinant Ψ_s and the calculation of its total electronic energy E^{KS} and the kinetic, nuclear-attraction and Coulomb repulsion components T_s, V, W_H as well as the (DFT) exchange energy E_x and correlation energy E_c. Comparison of these DFT quantities has been made on one hand with the corresponding Hartree–Fock (HF) quantities and on the other hand with local density approximation (LDA) and generalized gradient approximation (GGA). Comparison with HF shows that the correlation errors in the components T, V, and W_H of the total energy are much larger for HF than KS determinantal wave functions. However, the total energies E^{KS} and E^{HF} appear to be close to each other, as well as the exchange energies E_x and E_x^{HF} and correlation energies E_c and E_c^{HF}. The KS determinantal wave function and the KS orbitals therefore correspond to much improved kinetic and Coulombic energies, while having only a slightly larger total correlation energy. It is stressed that these properties of the Kohn–Sham orbitals make them very suitable for use in the molecular orbital theories of chemistry. Comparison of the accurate Kohn–Sham exchange and correlation energies with LDA and GGA shows that the GGA exchange energies are consistently too negative, while the GGA correlation energies are not negative enough. It is argued that the GGA exchange functionals represent effectively not only exchange, but also the molecular non-dynamical correlation, while the GGA correlation functionals represent dynamical correlation only. © *1997 American Institute of Physics.* [S0021-9606(97)00337-1]

I. INTRODUCTION

The exchange-correlation energy E_{xc} of a many-electron system is the key quantity of density functional theory (DFT).[1–3] Within the Kohn–Sham (KS) theory[4] E_{xc} is defined as a functional of the electron density ρ in the KS expression for the total electronic energy $E[\rho]$,

$$E[\rho]=T_s[\rho]+V[\rho]+W_H[\rho]+E_{\mathrm{xc}}[\rho], \tag{1.1}$$

where T_s is the kinetic energy of a noninteracting particle system with density ρ, V is the energy of electron–nuclear attraction, and W_H is the Coulomb or Hartree energy. E_{xc} can be further subdivided into the exchange E_x and correlation E_c energies

$$E_{\mathrm{xc}}[\rho]=E_x[\rho]+E_c[\rho]. \tag{1.2}$$

Accurate values of the exchange and correlation energies obtained for chemically interesting systems are essential for analysis of the effect of electron correlation within KS theory and in order to test and calibrate various DFT approximations. We emphasize that the DFT quantities E_x and E_c are not the traditional exchange and correlation energies of quantum chemistry, whose definition is tied to the Hartree–Fock (HF) model (see below).

Since the exact functional form of E_{xc} is not known, one can, in principle, determine accurate values of E_x and E_c from highly accurate *ab initio* wave functions, for example, from extensive configuration interaction (CI) calculations. From the accurate density ρ the Kohn–Sham orbitals ϕ_i corresponding uniquely to that density have to be determined in order to calculate E_x and E_c (see the next section for the corresponding formulas). The determination of the accurate KS orbitals $\phi_{i\sigma}(\mathbf{r})$ and the potential $v_s(\mathbf{r})$ from a given density ρ appears to be a complicated problem which was treated in a number of papers.[5–11] The systematic KS solutions for atoms from Li to Ar have been obtained relatively recently[12] followed by the first examples of molecular KS solutions.[13–16]

Because of the lack of accurate KS solutions, traditional Hartree–Fock based exchange and correlation energies have been used in DFT to obtain reference E_x and E_c values. In particular, E_x is approximated with the corresponding HF exchange energy E_x^{HF},

$$E_x \approx E_x^{\mathrm{HF}}, \tag{1.3}$$

while E_c of DFT is approximated with the difference E_c^{HF}

between the empirical total nonrelativistic electronic energy of a system E obtained from the spectroscopic data[17–19] and the HF electronic energy E^{HF},

$$E_c \approx E_c^{\mathrm{HF}} = E - E^{\mathrm{HF}}. \tag{1.4}$$

As has been pointed out before[20,21] (see also the next section) the definition of E_c in DFT differs conceptually from the definition of E_c^{HF} of traditional quantum chemistry. However, the HF method yields rather accurate electron densities for most atoms, and in those cases E_x and E_x^{HF} as well as E_c and E_c^{HF} are actually very close to each other.[22] In case of strong near-degeneracy correlation, such as in dissociating molecules, the HF and exact densities may differ strongly and the difference between the conventional and DFT definitions of exchange and correlation energies becomes relevant.[23,24] For molecules at the equilibrium geometry the question whether the DFT and traditional definitions produce close values of the exchange and correlation energies remains open.

In this paper the KS orbitals ϕ_i and energies such as T_s, E_x, E_c and others are obtained from *ab initio* wave functions for the homonuclear diatomic closed-shell molecules Li_2, N_2, F_2 at the equilibrium and elongated bond distances. These molecules are considered as prototype systems with truly covalent bonds and they are included into any representative set of molecules to check the accuracy of approximations in DFT. They represent rather different cases of covalent bonding, ranging from the weakly bonded Li_2 with a single $2s$-based σ bond, to the very strongly bonded N_2 with one σ and two π bonds, to the weakly bonded F_2 with one $2p$-based σ bond and Pauli repulsion between two p_π lone pairs on each F atom. A comparative analysis of the exchange and correlation energies of DFT and traditional quantum chemistry is performed using a partitioning of the KS and HF electronic energies E^{KS}, E^{HF} and correlation energies E_c, E_c^{HF} into various components. The values of the DFT exchange and correlation energies obtained are compared with those calculated with the GGA models of Becke,[25] and of Perdew and Wang[26–28] for exchange and of Perdew and Wang,[26–28] and of Lee, Yang, and Parr[29] for Coulomb correlation. As will be shown below, based on this comparison and on qualitative physical considerations one can arrive at the conclusion that for molecules the GGA exchange functionals take effectively into account also a part of the correlation energy corresponding to nondynamical correlation, while the GGA correlation functionals lack this part, thus representing the effect of dynamical correlation.

II. DEFINITION OF THE EXCHANGE AND CORRELATION ENERGIES IN DFT

In order to subdivide the exchange-correlation energy of DFT into the exchange E_x and correlation components [Eq. (1.2)], the determinantal wave function Ψ_s built from the KS orbitals ϕ_i is used as a reference function. By definition, these orbitals yield the true ground state density ρ

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 \tag{2.1}$$

so the energy E^{KS} of Ψ_s

$$E^{\mathrm{KS}} = \langle \Psi_s | \hat{H} | \Psi_s \rangle = T_s + V + W_H + E_x \tag{2.2}$$

($\hat{H}$ is the Hamiltonian of the system) includes the first three terms of Eq. (1.1). The fourth term in the right-hand side of Eq. (2.2) is the DFT definition for the exchange energy E_x,

$$E_x = -\frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 \times \frac{\phi_{i\sigma}^*(\mathbf{r}_1)\phi_{j\sigma}(\mathbf{r}_1)\phi_{j\sigma}^*(\mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{2.3}$$

where σ is the spin index. Actually, E_x has the same form, as a functional of the orbitals, as the Hartree–Fock (HF) exchange energy E_x^{HF} but $E_x[\rho]$ is defined with the KS orbitals ϕ_i related to the exact density $\rho(\mathbf{r})$, while E_x^{HF} is defined with the HF orbitals related to the HF density $\rho^{\mathrm{HF}}(\mathbf{r})$.

The DFT and traditional definitions of the correlation energy differ much more markedly. In DFT the correlation energy E_c is defined as the remainder when the exchange energy E_x defined above is subtracted from E_{xc}, which implies that E_c is simply the difference between the exact energy E of Eq. (1.1) and E^{KS} of Eq. (2.2),

$$E_c = E_{\mathrm{xc}} - E_x = E - E^{\mathrm{KS}}, \tag{2.4}$$

so the KS determinantal wave function plays a role as reference wave function here in the same way as the HF determinantal wave function does in the conventional definition. Since the HF determinant is by definition the one with the lowest possible energy, the DFT correlation energy E_c is necessarily more negative (larger in an absolute sense) than the traditional correlation energy[30]

$$E_c \leqslant E_c^{\mathrm{HF}}. \tag{2.5}$$

E_c can be subdivided into the kinetic T_c and the potential W_c components,

$$E_c = [T - T_s] + [W_{\mathrm{xc}} - E_x] = T_c + W_c, \tag{2.6}$$

where W_{xc} is the exchange-correlation part of the exact electron–electron interaction energy W, $W_{\mathrm{xc}} = W - W_H$. On the other hand, according to the traditional definition, the correlation energy E_c^{HF} is the difference between E and the Hartree–Fock energy,

$$\begin{aligned} E_c^{\mathrm{HF}} &= E - E^{\mathrm{HF}}, \\ &= T - T^{\mathrm{HF}} + \int \Delta\rho(\mathbf{r})\nu(\mathbf{r})d\mathbf{r} + \int \frac{\Delta\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad + \frac{1}{2} \int \frac{\Delta\rho(\mathbf{r}_1)\Delta\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + W_{\mathrm{xc}} - E_x^{\mathrm{HF}} \\ &= T_c^{\mathrm{HF}} + V_c^{\mathrm{HF}} + W_{H,c}^{\mathrm{HF}} + W_c^{\mathrm{HF}}. \end{aligned} \tag{2.7}$$

The definitions (2.4) and (2.7) differ conceptually from each other, since the DFT correlation energy is a functional of the

exact density ρ, while the traditional one involves the difference $\Delta\rho=\rho-\rho^{\mathrm{HF}}$. Therefore correlation terms like V_c^{HF}, the correlation correction to the electron–nuclear attraction energy, and $W_{H,c,}^{\mathrm{HF}}$, the correlation correction to the Hartree energy of the electrostatic electron repulsion, do not enter E_c. Moreover, the terms T_c^{HF} and W_c^{HF} of E_c^{HF} will be different from the corresponding terms T_c and W_c of E_c. Note that W_c^{HF}, according to

$$W_c^{\mathrm{HF}}=W_{\mathrm{xc}}-E_x^{\mathrm{HF}}=E_x+W_c-E_x^{\mathrm{HF}}=\Delta E_x^{s,\mathrm{HF}}+W_c, \quad (2.8)$$

differs from W_c only in the difference $\Delta E_x^{s,\mathrm{HF}}$ between the KS and HF exchange energies.

In the next section the procedure employed to obtain the KS quantities will be outlined.

III. CALCULATION OF THE KS QUANTITIES

The procedure used in this paper to obtain the Kohn–Sham orbitals and energies from *ab initio* wave functions has been already presented and discussed in Refs. 31,14. To obtain the correlated wave functions, the HF and subsequent CI calculations have been performed for the ground states by means of the ATMOL package[32] at the bond distances $R_e=5.05$, $R=6.0$, and $R=7.0$ a.u. for Li_2; $R_e=2.074$, $R=3.0$, and $R=3.5$ a.u. for N_2; $R_e=2.668$, $R=3.0$, and $R=3.5$ a.u. for F_2. A basis of contracted Gaussian functions has been used for the calculations. For Li a basis[33] with eight s- and four p-type functions has been used, which has been augmented with extra p and d polarization functions. For N and F the correlation-consistent polarized core-valence triple zeta added (cc-pCVTZ) basis sets[34] have been used.

The basis sets cc-pCVXZ from X=D (double zeta) to X=Q (quintuple zeta) were obtained for the atoms B through Ne as an extension of the correlation-consistent polarized valence basis sets (cc-pVXZ).[35] This extension allows us to represent adequately the correlated electron density ρ in all regions and to treat uniformly core, core–valence, and valence correlation effects when performing the multireference CI (MRCI) calculations with the cc-pCVXZ basis. This goal is achieved by the inclusion of a large number of basis functions, so that the gap between the core and valence exponents is rather small.[34] The exponents were optimized in atomic MRCI calculations. In order to describe properly effects of angular core and valence electron correlation, higher angular momentum polarization functions were included with both high exponents (corelike) and intermediate exponents (valence size). In particular, the cc-pCVTZ basis chosen in this paper includes p- and d-type polarization functions of typical core extent and d- and f-type polarization functions with typical valence exponents. In a similar way, in order to describe properly the angular correlation, we have augmented the basis of Ref. 33 for Li with polarization p- and d-type functions of both core and valence extent.

The performance of MRCI with the combined cc-pCVXZ basis sets as well as with the original cc-pVXZ sets was tested in Refs. 34, 36, 37 in atomic calculations and with benchmark calculations on the H_2, C_nH $(n=2-7)$, OH, HF, N_2 molecules. MRCI calculations in the cc-pCVXZ basis have proven to provide the same good description of the valence correlation effects as the corresponding calculations in a basis of atomic natural orbitals (ANO).[38] In general, the quality of the results appreciably improves when going from cc-pCVDZ to cc-pCVTZ basis, while further extension of the basis produces relatively little improvement. The test MRCI calculations in the cc-pCVTZ basis reproduce well the state separation energies, equilibrium geometry, harmonic frequencies, and anharmonicities, as well as the dipole and quadrupole moments, which is indicative of the good quality of the corresponding wave function and the correlated density ρ.

In this paper the MRCI calculations have been carried out within the direct CI approach with 106 reference configurations for Li_2 and N_2 and 36 reference configurations for F_2. The reference configurations were selected within the internal space of eight lowest energy Hartree–Fock molecular orbitals (MO) for Li_2 and 10 orbitals for N_2 and F_2. For N_2 and F_2 the internal space includes, apart from the occupied orbitals of the main (Hartree–Fock) configuration, also the orbitals, which are essential for a proper dissociation limit of the molecule. These are the $2p_\sigma^*$-MO of F_2 and $2p_\sigma^*$-, $2p_\pi^*$-MOs of N_2. For Li_2, apart from $1s_\sigma$, $1s_\sigma^*$-, $2s_\sigma$, and $2s_\sigma^*$-MOs (the inclusion of the latter MO is essential for a proper dissociation limit), three more σ-type and two π-type orbitals have been included into the internal space. This choice of the internal space for the reference configurations together with the use of the cc-pCVTZ basis is expected to provide a reliable description of the correlated ρ at both equilibrium and larger bond distances $A-A$.

All single and double excitations from each reference configuration to either internal or external subspaces have been included in the MRCI, which have also been augmented with the configurations obtained by single excitation from a reference configuration to the internal subspace with subsequent single excitation to the external subspace. The MRCI calculations performed at R_e recover 86% of the total Coulomb correlation energy E_c^{HF} for Li_2 and N_2, and 84% of E_c^{HF} for F_2.

The KS orbitals $\phi_i(\mathbf{r})$ and potential $\nu_s(\mathbf{r})$ of the one-electron KS equations,

$$[-\tfrac{1}{2}\nabla^2+\nu_s(\mathbf{r})]\phi_i(\mathbf{r})=\epsilon_i\phi_i(\mathbf{r}) \quad (3.1)$$

have been obtained with an iterative procedure,[11] which has been used previously to calculate the exchange-correlation potentials and energy densities for the monohydrides LiH, BH, HF.[13,14] The KS orbitals ϕ_i are represented in the same basis of MO's as has been used for the MRCI calculations. The accuracy of the resultant KS solution can be characterized with the values of the integrated difference between the calculated and target densities (absolute integral error of the iterative procedure) $\Delta\rho=0.0035$ e for N_2, $\Delta\rho=0.007$ e for F_2, and $\Delta\rho=0.04$ e for Li_2 obtained at R_e after 100 iterations. The relatively large error for Li_2 appears, probably, because for this molecule with its diffuse electron density the region of density tails (where both the Gaussian basis set representation and the potential construction procedure are

TABLE I. Kohn–Sham energy characteristics (a.u.) for Li_2 and their differences from the Hartree–Fock characteristics.

R(Li–Li)	5.05	6.0	7.0
T_s	14.902	14.840	14.817
$\Delta T^{s,\mathrm{HF}}$	0.011	0.015	0.036
T_c	0.083	0.084	0.079
T_c^{HF}	0.094	0.099	0.115
V	−38.062	−37.392	−36.880
$\Delta V^{s,\mathrm{HF}}=V_c^{\mathrm{HF}}$	−0.048	−0.044	−0.064
W_H	10.079	9.729	9.450
$\Delta W_H^{s,\mathrm{HF}}=W_{H,c}^{\mathrm{HF}}$	0.045	0.032	0.037
E_x	−3.565	−3.541	−3.521
$\Delta E_x^{s,\mathrm{HF}}$	−0.002	0.001	0.001
W_c	−0.194	−0.190	−0.192
W_c^{HF}	−0.196	−0.190	−0.192
E_c	−0.111	−0.106	−0.113
E_c^{HF}	−0.105	−0.103	−0.104
$\Delta E_c^{s,\mathrm{HF}}$	−0.006	−0.03	−0.009
E_c^{emp}	−0.128		

TABLE III. Kohn–Sham energy characteristics (a.u.) for F_2 and their differences from the Hartree–Fock characteristics.

R(F–F)	2.668	3.0	3.5
T_s	198.922	198.754	198.726
$\Delta T^{s,\mathrm{HF}}$	0.356	0.436	0.545
T_c	0.450	0.454	0.454
T_c^{HF}	0.806	0.890	0.999
V	−537.656	−530.896	−523.252
$\Delta V^{s,\mathrm{HF}}=V_c^{\mathrm{HF}}$	−0.493	−0.653	−0.890
W_H	129.566	126.286	122.529
$\Delta W_H^{s,\mathrm{HF}}=W_{H,c}^{\mathrm{HF}}$	0.122	0.215	0.363
E_x	−19.935	−19.841	−19.760
$\Delta E_x^{s,\mathrm{HF}}$	0.024	0.022	0.014
W_c	−1.082	−1.122	−1.181
W_c^{HF}	−1.058	−1.101	−1.167
E_c	−0.632	−0.668	−0.727
E_c^{HF}	−0.623	−0.649	−0.695
$\Delta E_c^{s,\mathrm{HF}}$	−0.009	−0.019	−0.032
E_c^{emp}	−0.755		

less adequate) plays a more important role. The errors $\Delta\rho$ increase with increasing bond distance $R(A-A)$. Finally, using *ab initio* energies and densities as well as the obtained KS orbitals, the exchange and correlation energies and their components have been calculated. They will be presented and discussed in the next section.

IV. CORRELATION CORRECTIONS TO THE KINETIC ENERGY AND VARIOUS POTENTIAL ENERGY TERMS FOR THE KOHN–SHAM AND HARTREE–FOCK DETERMINANTAL WAVE FUNCTIONS

Tables I–III present various Kohn–Sham energy characteristics of Li_2, N_2, and F_2 calculated for three different bond distances $R(A-A)$. The components T_s, V, W_H, and E_x of the total electronic energy E^{KS}, all calculated with the KS determinant Ψ_s, and the KS correlation energy $E_c=T_c+W_c$ [Eq. (2.6)] are compared with those calculated with the Hartree–Fock determinant and the corresponding differences $\Delta E_i^{s,\mathrm{HF}}$ are presented. The HF determinant differs markedly from the KS determinant, in particular for N_2 and F_2, as can be judged from the large differences $\Delta T^{s,\mathrm{HF}}$, $\Delta V^{s,\mathrm{HF}}$, $\Delta W_H^{s,\mathrm{HF}}$ in the kinetic energy, electron–nuclear and Hartree part of the electron–electron potential energy, respectively. The magnitude of these terms may be put in perspective when comparing them to the dissociation energies of these molecules which range from a few hundredths of an a.u. (Li_2 and F_2) to ~0.37 a.u. (N_2). The explanation of the large differences between these KS and HF quantities is the diffuse nature of the HF orbitals and electron density.[39,24] The Coulomb correlation leads to a considerable contraction of the correlated density ρ around the nuclei as compared with the HF one, ρ^{HF}. Because of this contraction, the corresponding differences of the electron–nuclear attraction energies $\Delta V^{s,\mathrm{HF}}=V-V^{\mathrm{HF}}$ are in all cases negative, while those of the kinetic energy, $\Delta T^{s,\mathrm{HF}}=T_s-T^{\mathrm{HF}}$, and the Hartree energy, $\Delta W_H^{s,\mathrm{HF}}=W_H-W_H^{\mathrm{HF}}$, are positive. Obviously, since the KS density is exact, there are no correlation corrections to the KS V and W_H, and $\Delta V^{s,\mathrm{HF}}$ and $\Delta W_H^{s,\mathrm{HF}}$ also represent the HF correlation corrections V_c^{HF} and $W_{H,c}^{\mathrm{HF}}$ to V and W_H. The large $\Delta W_H^{s,\mathrm{HF}}$ and $\Delta V^{s,\mathrm{HF}}$ in the tables demonstrate the large correlation corrections in the electron–electron and in particular in the electron–nuclear Coulombic energies in the case of HF. They are as a matter of fact of the same order of magnitude as W_c and W_c^{HF}, which represent the change in the electron–electron interaction energy due to the Coulomb hole. W_c is purely an effect of the correlation between the electrons, but it is not significantly larger than the ''secondary'' effects of the correlation induced changes in the one-electron density matrix and diagonal density, T_c^{HF}, V_c^{HF}, and $W_{H,c}^{\mathrm{HF}}$, respectively. The T_c and T_c^{HF} values are given explicitly in the tables and show that these correlation corrections to the kinetic energies are modest as a percentage of T, but they are large in an absolute sense, and they differ significantly (about a factor 2 for N_2 and F_2) between KS and HF.

In view of the considerable differences between various

TABLE II. Kohn–Sham energy characteristics (a.u.) for N_2 and their differences from the Hartree–Fock characteristics.

R(N–N)	2.074	3.0	3.5
T_s	109.070	108.095	108.223
$\Delta T^{s,\mathrm{HF}}$	0.296	0.692	0.903
T_c	0.329	0.328	0.313
T_c^{HF}	0.625	1.020	1.216
V	−303.628	−288.260	−283.780
$\Delta V^{s,\mathrm{HF}}=V_c^{\mathrm{HF}}$	−0.558	−1.330	−1.759
W_H	75.068	67.858	65.666
$\Delta W_H^{s,\mathrm{HF}}=W_{H,c}^{\mathrm{HF}}$	0.274	0.716	0.980
E_x	−13.114	−12.621	−12.490
$\Delta E_x^{s,\mathrm{HF}}$	−0.006	−0.040	−0.067
W_c	−0.804	−0.969	−1.063
W_c^{HF}	−0.810	−1.009	−1.124
E_c	−0.475	−0.641	−0.750
E_c^{HF}	−0.469	−0.603	−0.687
$\Delta E_c^{s,\mathrm{HF}}$	−0.006	−0.038	−0.063
E_c^{emp}	−0.552		

HF and KS energy terms, it is quite remarkable to note that in a number of cases there is close agreement. To begin with, the exchange energies E_x and E_x^{HF} are quite close for $R_e(A-A)$ (note the small $\Delta E_x^{s,\mathrm{HF}}$ in the tables) except for F_2. As a consequence W_c and $W_c^{\mathrm{HF}}=\Delta E_x^{s,\mathrm{HF}}+W_c$ are quite close. Since on the other hand T_c and T_c^{HF} differ quite a bit, one would expect $E_c=T_c+W_c$ to differ from E_c^{HF}, but remarkably the remaining terms V_c^{HF} and $W_{H,c}^{\mathrm{HF}}$ in E_c^{HF} [see Eq. (2.7)] are not only individually large but also cancel the difference in T_c and T_c^{HF}, so that ultimately E_c and E_c^{HF} are very close. The difference $\Delta E_c^{s,\mathrm{HF}}$ between E_c and E_c^{HF} is simply the difference between the energies E^{HF} and E^{KS}, as follows immediately from Eqs. (2.4) and (2.7),

$$\Delta E_c^{s,\mathrm{HF}}=E_c-E_c^{\mathrm{HF}}=E^{\mathrm{HF}}-E^{\mathrm{KS}} \tag{4.1}$$

and E^{HF} and E^{KS} are probably close due to the stationarity of the HF determinantal energy against orbital variation. As was noted before, the HF determinant is by definition the one with the lowest possible energy [cf. Eq. (2.5)], and $\Delta E_c^{s,\mathrm{HF}}$ is always negative (see Tables I–III).

We use the calculated $\Delta E_c^{s,\mathrm{HF}}$ values to estimate the true correlation energies E_c of DFT for Li_2, N_2, F_2. In order to do this, we add the difference $\Delta E_c^{s,\mathrm{HF}}$ to the empirical value for the traditional correlation energy $E_c^{\mathrm{HF,emp19}}$ obtained by using an empirical estimate for the exact total energy E in the equation below,

$$E_c^{\mathrm{emp}}=(E^{\mathrm{emp}}-E^{\mathrm{HF}})+(E^{\mathrm{HF}}-E^{\mathrm{KS}})=E_c^{\mathrm{HF,emp}}+\Delta E_c^{s,\mathrm{HF}}. \tag{4.2}$$

As follows from the previous discussion, the resulting empirical E_c^{emp} values presented in Tables I–III are close to the corresponding $E_c^{\mathrm{HF,emp}}$ ones. One can conclude that the present results for $R_e(A-A)$ justify (at least, for the case of the second row dimers) the current practice to approximate the DFT quantities E_x and E_c with the traditional E_x^{HF} and E_c^{HF} ones.

However, for larger bond distances $R(A-A)$ this conclusion does not hold true. The quality of the HF density ρ^{HF} deteriorates with increasing bond distance and it becomes progressively less contracted than the correlated density ρ. This is due to the ionic configurations present in the covalent bonds described by the RHF wave function. The Hartree–Fock effective field is therefore too repulsive around the nuclei, an effect that is particularly strong at large bond lengths and if there are ionic configurations with multiple charge, as is inevitable in case of multiple bonds.[40] As a result, the differences $\Delta T^{s,\mathrm{HF}}$, $\Delta V^{s,\mathrm{HF}}$, $\Delta W_H^{s,\mathrm{HF}}$ increase, quite significantly so for N_2 and F_2, and moderately for Li_2 [$\Delta W_H^{s,\mathrm{HF}}$ for Li_2 actually slightly decreases for larger distances $R(\mathrm{Li–Li})=6.0$ and 7.0 a.u.]. Compensation of the differences in the various terms which have opposite sign again takes place in these cases to a high degree, yet the resulting $\Delta E_c^{s,\mathrm{HF}}$ values are distinctly more negative than those for $R_e(A-A)$, so that the DFT correlation energy E_c becomes progressively more negative than the traditional E_c^{HF}.

Left–right correlation is treated fundamentally differently in KS and HF calculations[41,24] (it is not treated at all in the latter case). The progressively larger V_c^{HF} and $W_{H,c}^{\mathrm{HF}}$ values upon bond lengthening reflect the increasingly more diffuse nature of the HF orbitals due to the presence of ionic configurations. There are no corresponding correlation errors in V and W in the KS case. A similar important difference between HF and KS is apparent in the kinetic energies. Tables I–III present the kinetic part of the DFT exchange-correlation energy T_c as well as that of the traditional correlation energy T_c^{HF}. The T_c and T_c^{HF} values are evaluated as the difference between the CI kinetic energy T^{CI} and the corresponding independent-particle kinetic energies,

$$T_c\approx T^{\mathrm{CI}}-T_s, \tag{4.3}$$

$$T_c^{\mathrm{HF}}\approx T^{\mathrm{CI}}-T^{\mathrm{HF}}. \tag{4.4}$$

The diffuse nature of the HF orbitals makes T^{HF} increasingly lower than T^{CI}, i.e., T_c^{HF} increases strongly upon bond elongation, in particular in the triply bonded N_2, for which T_c^{HF} increases from 0.625 hartree at $R(\mathrm{N–N})=2.074$ a.u. to 1.216 hartree at $R(\mathrm{N–N})=3.5$ a.u. The kinetic energy of the KS system does not suffer such an error, and in fact T_c hardly changes as a function of bond distance. In the dissociation limit T_c approaches to the sum of the T_c contributions of the atomic fragments,[23] which does not appear to be much different from T_c at R_e.

To sum up, the results of this section show that for the dimers Li_2, N_2, F_2 at the equilibrium bond distances the DFT and the traditional definitions of the exchange and correlation energies produce close numerical values. However, these close values emerge from the nearly precise cancellation of large differences $\Delta T^{s,\mathrm{HF}}$, $\Delta V^{s,\mathrm{HF}}$, $\Delta W_H^{s,\mathrm{HF}}$ of the corresponding individual contributions. In other words, in spite of the abovementioned difference of the HF and KS electron densities, the electronic energy of the molecules A_2 calculated at the equilibrium bond distances in the exchange-only approximation (i.e., from the one-determinantal wave functions) remains practically the same for both HF and KS approaches. However, for the dissociating molecules, and in general for weak-interaction situations, the typical Hartree–Fock error of neglect of left–right correlation becomes more serious and the DFT and traditional definitions yield increasingly different exchange and correlation energies. The traditional exchange and correlation energies can no longer be taken as reference values for molecular DFT applications.

V. KS AND GGA EXCHANGE AND CORRELATION ENERGIES

The KS exchange energies E_x and the empirical estimate E_c^{emp} of the DFT correlation energies for Li_2, N_2, F_2 presented in the previous section are compared in Table IV with those calculated with the current functionals of the generalized gradient approximation (GGA) and also with the corresponding values obtained with the local density approximation (LDA).[42,43] In the last column of the table the exchange-correlation energy $E_x+E_c^{\mathrm{emp}}$ (row labeled KS) is compared with the sum of the exchange E_x^{PW} and correlation E_c^{PW} functionals of Perdew and Wang[26–28] (row PW/PW), the sum of the exchange E_x^B functional of Becke[25] and E_c^{PW} (row BPW), and the sum of E_x^B and the correlation functional E_c^{LYP} of

TABLE IV. Kohn–Sham, LDA, and GGA exchange and correlation energies (a.u.). The KS entries in the E_c and E_{xc} columns refer to the empirical estimates E_c^{emp} and $E_{xc}=E_x+E_c^{emp}$.

		E_x	E_c	E_{xc}
	LDA	−3.084	−0.330	−3.414
	PW/PW	−3.537	−0.137	−3.674
Li_2	BPW	−3.555	−0.137	−3.692
	BLYP	−3.555	−0.134	−3.699
	KS	−3.565	−0.128	−3.693
		$E_x+E_c^{nd}$:	$E_c-E_c^{nd}$:	
		−3.574	−0.119	
	LDA	−11.873	−0.942	−12.815
	PW/PW	−13.180	−0.490	−13.670
N_2	BPW	−13.208	−0.490	−13.698
	BLYP	−13.208	−0.484	−13.692
	KS	−13.114	−0.552	−13.666
		$E_x+E_c^{nd}$:	$E_c-E_c^{nd}$:	
		−13.190	−0.476	
	LDA	−18.211	−1.296	−19.507
	PW/PW	−20.066	−0.669	−20.735
F_2	BPW	−20.101	−0.669	−20.770
	BLYP	−20.101	−0.675	−20.776
	KS	−19.935	−0.755	−20.690
		$E_x+E_c^{nd}$:	$E_c-E_c^{nd}$:	
		−20.014	−0.676	
H_2 ($R_e=1.401$)	LDA	−0.569	−0.095	−0.664
	BPW	−0.658	−0.046	−0.704
	KS	−0.661	−0.039	−0.700
		$E_x+E_c^{nd}$:	$E_c-E_c^{nd}$:	
		−0.662	−0.038	
H_2 ($R_e=5.0$)	LDA	−0.423	−0.083	−0.506
	BPW	−0.512	−0.032	−0.544
	KS	−0.410	−0.186	−0.596
		$E_x+E_c^{nd}$:	$E_c-E_c^{nd}$:	
		−0.524	−0.072	

Lee, Yang and Parr[29] (row BLYP). In the first and second columns the KS E_x and E_c^{emp}, respectively, are compared with the corresponding individual components of PW/PW, BPW, and BLYP. All LDA and GGA values are calculated at the equilibrium bond distances with the same *ab initio* density ρ, which has been used to obtain the KS solution.

For the LDA functionals the trend for all three molecules is rather uniform. The correlation functional of LDA tends to overestimate the molecular electron correlation by ~100% and E_c^{LDA} values are consistently too negative. This is due to the well-known difference in correlation between the homogeneous electron gas model (which is represented by the LDA) and finite inhomogeneous atomic and molecular systems[44] (the overestimation is corrected properly in the GGA correlation functionals). However, this overestimation is overcompensated by underestimation of the atomic and molecular exchange in LDA, so that E_x^{LDA} and the total E_{xc}^{LDA} values are significantly higher (less negative) than the corresponding KS ones.

The gradient corrections of GGA bring the corresponding exchange and correlation energies much closer to the KS ones as compared to LDA. In particular, for Li_2 the exchange energy E_x^B and the correlation energies E_c^{PW} and E_c^{LYP} are only a few millihartrees off their KS counterparts, with the difference between E_x^{PW} and E_x being somewhat larger. As a result, the corresponding GGA exchange-correlation energies are also close to the KS ones.

However, for N_2 and F_2 appreciable differences between the individual GGA and KS exchange and correlation components of the exchange-correlation energy are observed. Here, both GGA exchange functionals yield consistently too negative values as compared with the KS E_x. The largest difference is between E_x^B and E_x, amounting to −0.094 hartrees for N_2 and to −0.166 hartrees for F_2. On the other hand, the GGA correlation functionals yield consistently too high values as compared with E_c^{emp}. For N_2 the largest difference of 0.068 hartrees is for E_c^{LYP} and for F_2 the largest difference of 0.086 hartrees is for E_c^{PW}. These differences of opposite signs compensate each other to a large extent in the resulting GGA exchange-correlation energies. For N_2 the PW value $E_{xc}^{PW}=-13.67$ hartrees practically coincides with the corresponding KS value $E_x+E_c^{emp}=-13.666$ hartrees and the BPW and BLYP values are not very far from $E_x+E_c^{emp}$. For F_2 there is also considerable compensation of errors of opposite sign in E_x and E_c, but a somewhat larger difference between the KS and GGA values for E_{xc} remains (see Table IV).

Note, that according to Ref. 45, the deviation of the atomization energy of the N_2 molecule calculated with the PW approximation from the empirical atomization energy is 0.021 hartrees. Its sign indicates relative overestimation of the molecular total energy within the PW GGA, in agreement with the abovementioned overestimation of the exchange-correlation energy of this molecule (E_{xc}^{PW} is 0.004 hartrees lower than $E_x+E_c^{emp}$), but the absolute value of the atomization energy error of PW is larger than that of the molecular exchange-correlation energy error. A possible reason for this might be a slight relative underestimation of the total energy of the N atom with the PW GGA. Another reason is that calculations with the PW functional have been carried out in this paper and in Ref. 45 with different densities ρ. While in Ref. 45 ρ obtained with the local spin density approximation has been used, in this paper the MRCI ρ has been employed to calculate E_{xc}^{PW}.

We have observed in a study of the correlation energy density $\epsilon_c(\mathbf{r})$ Ref. 31 for dissociating H_2 that the GGA lacks the left–right correlation. This is also evident from the large error in W_c^{PW} as compared to the exact W_c in the same case[23] (−0.057 instead of −0.207 at $R=5.0$ bohr). The trouble stems from the fact that the LDA and GGA approximations do not properly describe exchange and correlation separately. This may be understood from the exchange (Fermi) and correlation (Coulomb) hole functions $\rho_x(\mathbf{r}_2|\mathbf{r}_1)$ and $\rho_c(\mathbf{r}_2|\mathbf{r}_1)$ from which the corresponding energies may be obtained

$$E_x=\frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho_x(\mathbf{r}_2|\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|}\,d\mathbf{r}_1 d\mathbf{r}_2, \tag{5.1}$$

$$W_c=\frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho_c(\mathbf{r}_2|\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|}\,d\mathbf{r}_1 d\mathbf{r}_2. \tag{5.2}$$

If the reference position $\mathbf{r}_1$ is close to nucleus A of a diatomic AB, the exchange and correlation holes will be delocalized over both centers, irrespective of their distance. This delocalization is unphysical, and in fact the exchange and correlation holes on center B have opposite sign and cancel each other. They are both negative at A and build together a localized hole at A around the reference position $\mathbf{r}_1$. (We refer to Ref. 39 for an extensive discussion of the shape and behavior of exchange and correlation holes.) The electron gas does not contain the phenomenon of left–right correlation, the holes are always localized around the reference electron. The exchange and correlation functionals developed from the homogeneous or inhomogeneous electron gas cannot be expected to be able to describe the corresponding delocalized holes in molecules. However, it is an old notion[46] that the exchange functional, since it mimicks a localized hole, might be hoped to be describing in molecules the combined effect of exchange and left–right correlation, which also leads to a localized hole (cf. also Ref. 47).

It is the so-called nondynamical or near-degeneracy correlation that introduces left–right correlation and effects the hole localization. The LDA and GGA functionals cannot describe the exact KS exchange, since it has a delocalized hole, but it is interesting to investigate to what extent the LDA or GGA exchange functionals effectively describe, even if not by construction, the combined effect of exchange and nondynamical correlation. Dynamical correlation alone might be described by the electron-gas based correlation functionals. The energy of nondynamical correlation E_c^{nd} can be estimated with the assumption that simple CI wave functions constructed in Ref. 33, which provide the proper dissociation limit (PDL) for the dimers A_2, take into account the effect of nondynamical correlation and neglect dynamical correlation. With this assumption the energy E_c^{nd} can be estimated as the difference between the electronic energies of the PDL and HF functions, $E_c^{\mathrm{nd}}=E^{\mathrm{PDL}}-E^{\mathrm{HF}}$. This yields E_c^{nd} values of -0.009, -0.076, and -0.079 hartrees for Li_2, N_2, and F_2, respectively. Thus, the energy effect of nondynamical correlation at $R_e(A–A)$ is small for Li_2, while it is appreciable for N_2 and F_2. Bearing this in mind, we present in Table IV the energy of dynamical correlation E_c^d estimated as the difference $E_c^d=E_c^{\mathrm{emp}}-E_c^{\mathrm{nd}}$ and the sum $(E_x+E_c^{\mathrm{nd}})$ of the exchange energy and E_c^{nd}. The energies E_c^d appear to be close to the GGA correlation energies,

$$E_c^{\mathrm{GGA}}\cong E_c^d. \tag{5.3}$$

Thus, we arrive at the conclusion that the GGA correlation functionals $E_c^{\mathrm{GGA}}[\rho]$ (E_c^{PW} or E_c^{LYP}) effectively model the dynamical correlation of electrons in N_2 and F_2. Similarly, the GGA ''exchange'' energies are actually much closer to the sum of exchange and nondynamical correlation energies,

$$E_x^{\mathrm{GGA}}\cong E_x+E_c^{\mathrm{nd}}. \tag{5.4}$$

The localized hole corresponding to $E_x^{\mathrm{GGA}}[\rho]$ simulates the abovementioned combined effect of exchange and nondynamical correlation which produces a localized exchange-correlation hole. For N_2 the GGA exchange energies (especially, the PW one) are close to the sum $(E_x+E_c^{\mathrm{nd}})$ (see Table IV). For F_2 the energies E_x^{GGA} are still too negative, but they are clearly much closer to $(E_x+E_c^{\mathrm{nd}})$ than to the bare exchange energy E_x. For Li_2, as was shown above, the effect of nondynamical correlation is small at R_e(Li–Li) and Eq. (5.4) reduces effectively within GGA to $E_x^{\mathrm{GGA}}\cong E_x$, while Eq. (5.3) reduces to $E_c^{\mathrm{GGA}}\cong E_c$. At elongated distances E_c^{nd} is expected to become much larger, but no E_c^{emp} is available. We have therefore added to Table IV entries for the well-studied case of H_2 at both equilibrium distance and at $R=5.0$ bohr, where we may rely on full-CI calculations to obtain accurate correlation energies. Full-CI results and E_c^{nd} from a proper-dissociation CI involving just the configurations $(\sigma_g)^2$ and $(\sigma_u)^2$ have been obtained from Ref. 39. E_c^{nd} is very small (-0.001 a.u.) at R_e, but at $R=5$ bohr it is of course large (-0.114 a.u.) for this prototype case of left–right correlation. There is a striking discrepancy at $R=5$ bohr between the PW estimate of E_c (-0.032) and the accurate KS value (-0.186). In this case the near-degeneracy part of E_c is large, and E_c^{PW} is clearly much closer to $E_c-E_c^{\mathrm{nd}}$. Also $E_x+E_c^{\mathrm{nd}}$ is closer to the Becke exchange energy than the bare KS exchange energy is. Since T_c is small at this large distance,[23] E_c is close to W_c, and we note that the large discrepancy observed in Ref. 23 between W_c and W_c^{PW} may be similarly explained by W_c^{PW} lacking the near-degeneracy part.

Summarizing, GGA appears to provide approximately the partitioning

$$E_{\mathrm{xc}}^{\mathrm{GGA}}=E_x^{\mathrm{GGA}}+E_c^{\mathrm{GGA}}\cong(E_x+E_c^{\mathrm{nd}})+E_c^d \tag{5.5}$$

for the exchange-correlation energy.

VI. CONCLUSIONS

In this paper the difference between the DFT definition of exchange and correlation and the traditional Hartree–Fock based one is stressed. In particular we have noted that the components T_s, V, and W_H of the KS energy differ significantly from their HF counterparts. The conceptual difference of the DFT and traditional definitions of the correlation energy is illustrated by the markedly different dependence of the corresponding kinetic components T_c and T_c^{HF} on the bond distance R(N–N). While T_c^{HF} rapidly increases with increasing R(N–N), T_c remains practically constant for the distances considered (cf. Ref. 48). However, at the equilibrium bond distances, due to compensation of differences of opposite sign, the total energies E^{KS} and E^{HF} of the KS and HF one-determinantal wave functions are close to each other, as are the corresponding exchange energies E_x and E_x^{HF}. As a result, E_c and E_c^{HF} values are also close to each other. These results justify for the equilibrium geometry the existing practice to assess the performance of approximate DFT exchange and correlation functionals for molecules by comparing to conventional E_x^{HF} and E_c^{HF} values. For elongated bond distances the difference between E_c and E_c^{HF} increases somewhat. For N_2, a molecule with a triple bond and strong Coulomb correlation effects, the difference between E_c and E_c^{HF} has increased to 10% at 3.5 bohr. It is therefore worthwhile to take into account the difference between the DFT

and traditional definitions of correlation if one tries to develop DFT functionals capable to calculate accurately full molecular potential energy surfaces.

The HF determinant is often denoted as the ''best'' one-determinantal wave function (and therefore the HF orbitals as the ''best'' orbitals) since it yields the lowest energy. However, it is to be noted that the HF wave function makes quite large errors in important energy terms such as the kinetic energy and the electron–nuclear and electron–electron Coulomb energies. In N_2 for instance, the electron–nuclear energy is not negative enough by 15 eV at R_e, and by almost 50 eV at 3.5 bohr (to be compared to a bond energy of 10 eV and to a zero error in this term for the KS determinant). HF is making this error, which results from a too diffuse density, since it can lower the kinetic energy by making the density (i.e., the orbitals) diffuse. However, this increases the error in the kinetic energy; the HF error in the kinetic energy is at R_e twice the error of the kinetic energy of the KS orbitals, and at 3.5 bohr the HF error is four times as large (more than 33 eV too low, whereas T_s is only 8.5 eV too low). In short, HF is only trying to minimize the *total* energy, and it will make large errors in individual energy components if it can lower the total energy, even if only barely. It has been noticed that this ''freedom'' of HF to distort the density and the orbitals, if only the energy decreases, may lead to a distorted picture of chemical bonding, for instance to localized orbitals (ionic bonds) whereas more accurate wave functions (CASSCF) yield a covalent picture.[40,49] One can turn the above argument about the ''distortion'' effected by HF around and note that the KS determinant manages to improve the kinetic energy and various Coulomb energy terms with respect to HF very much, with only a small rise of the total energy, and therefore the (total) correlation energy. If the criterium for ''best determinantal wave function'' would not only be based on the correlation error in the total energy, but would also take into account the correlation errors in the physically important energy components discussed above, the KS determinantal wave function is clearly ''better.''

It is not useful to argue about ''better or not,'' since this amounts to deciding on the best criterium, which may be a matter of taste, but it is important to note that the present results hold an important message concerning the status of Kohn–Sham orbitals as compared to Hartree–Fock orbitals. The Kohn–Sham approach has endowed chemistry and physics with a new set of one-particle wave functions (orbitals). The physical meaning of these orbitals has for some time remained somewhat obscure, and it is sometimes stated that one should not look for physical meaning or usefulnes, but consider these orbitals as mere mathematical constructs whose only meaning is to build the exact density. However, we wish to reiterate[21,50] that on the contrary the KS orbitals do make physical sense. This is a direct consequence of the form of the local potential $\nu_s(\mathbf{r})$ in which the KS electrons move,

$$\nu_s(\mathbf{r}) = \nu(\mathbf{r}) + \nu_H(\mathbf{r}) + \nu_x^{\mathrm{hole}}(\mathbf{r}) + \nu_c^{\mathrm{hole}}(\mathbf{r}) + \nu_{c,\mathrm{kin}}(\mathbf{r}) + \nu^{\mathrm{resp}}(\mathbf{r}). \tag{6.1}$$

The leading terms in ν_s, the external (i.e., nuclear) field $\nu(\mathbf{r})$, the electronic Coulomb (or Hartree) potential $\nu_H(\mathbf{r})$, and the potential of the exchange or Fermi hole, $\nu_x(\mathbf{r})$, cause the KS orbitals to be roughly similar to the Hartree–Fock orbitals, with usually a similar nodal pattern and one-electron energy distribution. However, ν_s also contains the potential of the Coulomb hole $\nu_c^{\mathrm{hole}}(\mathbf{r})$ (we do not discuss the less important contributions $\nu_{c,\mathrm{kin}}$ and ν^{resp}, cf. Refs. 51,52,14). It is $\nu_c^{\mathrm{hole}}(\mathbf{r})$ that builds the most important aspects of electron correlation (such as the left–right correlation in a two-center bond) into the effective potential of the KS electron. The HF model causes an electron, when being in an atomic region, to feel too much repulsion from the remaining electrons (HF has too much weight for ''ionic configurations,'' in particular at long bond distances), hence the too diffuse nature of the HF orbitals. This HF error is annihilated by $\nu_c^{\mathrm{hole}}(\mathbf{r})$, making the total field correspond to a proper localized exchange-correlation hole around the reference electron.[39] This prevents the orbitals and density from becoming distorted, as they sometimes are in the HF model (for instance too diffuse, or unduly localized at one end of the bond[40,49]), and results in the ''advantages'' of the KS orbitals noted above. These properties of the KS orbitals may also lead to superior performance (as compared to HF orbitals) in perturbation theoretic approaches to the electron correlation problem, or various types of CI approaches. In this respect also the realistic nature of the KS virtual orbitals will play a role; the KS virtual orbitals do not exhibit the artificial upshift and diffuse nature of the HF virtual orbitals, the one-electron energy differences $\Delta\epsilon = \epsilon_a - \epsilon_i$ between a virtual orbital a and an occupied orbital i are closely related to excitation energies. We wish to stress that the properties of the KS orbitals make them particularly suitable for use in the molecular orbital theories of chemistry.[53,54]

For atoms LDA is known to underestimate the exchange energy by roughly 10% and it overestimates the correlation energy by roughly 100%. The present examples demonstrate this to be true for molecules as well. The errors do not cancel precisely, the total LDA exchange-correlation energies are consistently too high (not negative enough) as compared to the sum $(E_x + E_c^{\mathrm{emp}})$. The gradient corrections bring the GGA exchange and correlation energies much closer to E_x and E_c^{emp}, but for N_2 and F_2 they seem to overcorrect and the GGA exchange energies are consistently too low (too negative), while the GGA correlation energies are too high as compared to E_x and E_c^{emp}, respectively. However, the differences of opposite sign compensate each other and the resulting GGA exchange-correlation energies are rather close (especially, in the case of N_2) to the sum $(E_x + E_c^{\mathrm{emp}})$.

Concerning the systematic deviations between the GGA and KS exchange and correlation energies separately, we have noted that qualitative considerations concerning the difference between Fermi and Coulomb holes in molecules and in the electron gas suggest that the GGA exchange functionals represent effectively not only exchange, but also the molecular nondynamical Coulomb correlation, while the GGA correlation functionals represent the dynamical Coulomb correlation. We have demonstrated that there is semiquanti-

tative evidence for this point of view. However, since the GGA models were derived from the inhomogeneous electron gas and (at least, some of them) are fitted for atoms, their proper representation of the molecular nondynamical correlation might appear somewhat accidental and the quality of the calculated total exchange-correlation energies may vary. This, indeed, happens in the case of F_2 (see Table IV) for which GGA seems to overestimate nondynamical correlation so that the GGA exchange-correlation energies (especially in the BPW and BLYP variants) appear to be too negative. Further improvement of the approximate DFT functionals may require the development of gradient- and Laplacian-dependent model functionals for the exchange-correlation energy, in which the exchange and correlation components are not separated from each other.

[1] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
[2] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to the Many-Body Problem* (Springer, Berlin, 1990).
[3] W. Kohn, A. D. Becke, and R. G. Parr, J. Phys. Chem. **100**, 12 974 (1996).
[4] W. Kohn and L. J. Sham, Phys. Rev. **140A**, 1133 (1965).
[5] C. O. Almbladh and A. C. Pedroza, Phys. Rev. A **29**, 2322 (1984).
[6] F. Aryasetiawan and M. J. Stott, Phys. Rev. B **34**, 4401 (1986).
[7] A. Nagy and N. H. March, Phys. Rev. A **39**, 5512 (1989).
[8] A. Görling, Phys. Rev. A **46**, 3753 (1992).
[9] Y. Wang and R. G. Parr, Phys. Rev. A **47**, R1591 (1993).
[10] Q. Zhao and R. G. Parr, Phys. Rev. A **46**, 2337 (1992).
[11] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).
[12] R. C. Morrison and Q. Zhao, Phys. Rev. A **51**, 1980 (1995).
[13] O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends. Phys. Rev. A **52**, 1870 (1995).
[14] O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, J. Chem. Phys. **104**, 8535 (1996).
[15] V. E. Ingamells and N. C. Handy, Chem. Phys. Lett. **248**, 373 (1996).
[16] D. J. Tozer, V. E. Ingamells, and N. C. Handy, J. Chem. Phys. **105**, 9200 (1996).
[17] E. R. Davidson, S. A. Hagstrom, S. J. Chakravorty, V. M. Umar, and C. F. Fischer, Phys. Rev. A **44**, 7071 (1991).
[18] S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. Fischer, Phys. Rev. A **47**, 3649 (1993).
[19] A. Savin, H. Stoll, and H. Preuss, Theor. Chim. Acta **70**, 407 (1986).
[20] E. K. U. Gross, M. Petersilka, and T. Grabo, in *Chemical Applications of Density Functional Theory*, edited by B. B. Laird, R. B. Ross, and T. Ziegler (American Chemical Society, Washington, D.C., 1996), Vol. 629, p. 42.
[21] E. J. Baerends, O. V. Gritsenko, and R. van Leeuwen, in *Chemical Applications of Density Functional Theory*, edited by B. B. Laird, R. B. Ross, and T. Ziegler (American Chemical Society, Washington, D. C., 1996), Vol. 629, p. 20.
[22] A. Görling and M. Ernzerhof, Phys. Rev. A **51**, 4501 (1995).
[23] O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, Int. J. Quantum Chem. **60**, 1375 (1996).
[24] E. J. Baerends and O. V. Gritsenko, J. Phys. Chem. **A101**, 5383 (1997).
[25] A. Becke, Phys. Rev. A **38**, 3098 (1988).
[26] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B **54**, 16 533 (1996).
[27] J. P. Perdew, in *Electronic Structure of Solids*, edited by P. Ziesche and H. Eschrig (Akademie, Berlin, 1991), p. 11.
[28] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[29] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[30] V. Sahni and M. Levy, Phys. Rev. B **33**, 3869 (1985).
[31] P. Süle, O. V. Gritsenko, A. Nagy, and E. J. Baerends, J. Chem. Phys. **103**, 10 085 (1995).
[32] V. R. Saunders and J. H. van Lenthe, Mol. Phys. **48**, 923 (1983).
[33] G. C. Lie and E. Clementi, J. Chem. Phys. **60**, 1275 (1974).
[34] D. E. Woon and T. H. Dunning, J. Chem. Phys. **103**, 4572 (1995).
[35] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1988).
[36] D. E. Woon, Chem. Phys. Lett. **244**, 45 (1995).
[37] D. E. Woon, T. H. Dunning, and K. A. Peterson, J. Chem. Phys. **104**, 5883 (1996).
[38] J. Almloef and P. R. Taylor, J. Chem. Phys. **86**, 4070 (1987).
[39] M. A. Buijse and E. J. Baerends, in *Electronic Density Functional Theory of Molecules, Clusters and Solids*, edited by D. E. Ellis (Kluwer Academic, Dordrecht, 1995), p. 1.
[40] M. A. Buijse and E. J. Baerends, J. Chem. Phys. **93**, 4129 (1990).
[41] O. V. Gritsenko and E. J. Baerends, Theor. Chim. Acta. **96**, 44 (1997).
[42] *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).
[43] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[44] H. Stoll, C. M. E. Pavlidou, and H. Preuss, Theor. Chim. Acta. **49**, 143 (1978).
[45] J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).
[46] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw–Hill, New York, 1974), Vol. 4.
[47] M. Cook and M. Karplus. J. Phys. Chem. **91**, 31 (1987).
[48] R. van Leeuwen, O. V. Gritsenko, and E. J. Baerends, *Density Functional Theory I. Functionals and Effective Potentials*, edited by R. F. Nalewajski, in *Topics in Current Chemistry* (Springer, Berlin, 1996), Vol. 180, p. 107.
[49] M. A. Buijse and E. J. Baerends, Theor. Chim. Acta. **79**, 389 (1991).
[50] E. J. Baerends, O. V. Gritsenko, and R. van Leeuwen, in *New Methods in Quantum Theory*, edited by C. A. Tsipis, V. S. Popov, D. R. Herschbach, and J. S. Avery, *NATO ASI Series, Series 3: High Technology* (Kluwer, Dordrecht, 1996), Vol. 8, p. 395.
[51] O. V. Gritsenko and R. van Leeuwen, and E. J. Baerends, J. Chem. Phys. **101**, 8955 (1994).
[52] O. V. Gritsenko and E. J. Baerends, Phys. Rev. A **54**, 1957 (1996).
[53] R. Hoffmann, Angew. Chem. Int. Ed. Eng. **21**, 711 (1982).
[54] T. A. Albright, J. K. Burdett, and M. Whangbo, *Orbital Interactions in Chemistry* (Wiley, New York, 1985).